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are generally improved on cross-linking. Among other properties, thermal expansion and heat capacity are lowered, and heat distortion temperature, tensile strength, and refractive index are raised. Glass-transition temperature increases with increasing cross-link density (26). The increase ΔT_g in glass-transition temperature can be approximated by the following relationship:

$$\Delta T_g = A\nu \tag{23}$$

where ν = moles of cross-links per gram of polymer and the constant A is of the order 10^4–10^5. For styrene–divinylbenzene polymerization ($A = 7 \times 10^4$), the elevation in T_g is 12°C for a cross-link density change of 10^{20} cross-links per gram of polymer. For natural rubber cross-linked with dicumyl peroxide, ΔT_g is 6°C for the same change in cross-link density (27).

If a material is cured (cross-linked) isothermally at cure temperature T_{cure}, the rise in T_g reduces the chain mobility, and as T_g approaches T_{cure} the reaction may become diffusion controlled and eventually stop as the system undergoes vitrification (28). Complete cure is therefore obtained by curing at a temperature that is above the ultimate glass-transition temperature $T_{g\infty}$ of the system (29). Isothermal time–temperature–transformation (TTT) diagrams may be used to describe the various stages of cure in a thermosetting polymer (see CURING). Figure 5 shows a TTT diagram indicating regions of ungelled glass, liquid, gelled glass, gelled rubber, and char (30). At a very high temperature, the material decomposes to form char. Although the chemical reaction is extremely slow below T_g, sufficient reaction can take place over longer periods of time so that upon aging (qv) T_g may rise to 40°C above T_{cure}.

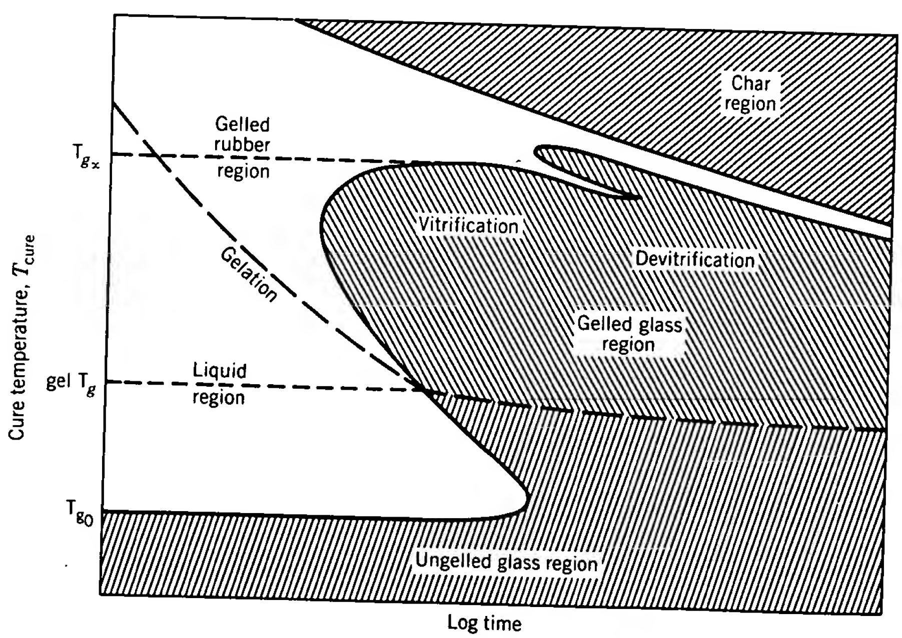

Fig. 5. Time–temperature–transformation (TTT) diagram.